

RESISTANCE TO ATMOSPHERIC CORROSION OF LOW-CARBON STEEL GRADE WT St 37-2

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Examination of low-carbon steel resistant to atmospheric corrosion has been actualized as a problem for a large number of years. Indeed, these steels have large importance for civil engineering structures, which will be exposed to changeable atmospheric conditions in next decades or centuries. Since the pollution of atmosphere is more evident nowadays, i.e. more aggressive, the importance of such examination is very significant. This is important for the selection of more suitable materials, as well as for the safety of structures, including the realisation of essential economic effects.

Key words: *low-carbon steel, atmospheric corrosion, resistance to atmospheric corrosion*

Otpornost na atmosfersku koroziju niskougličnog čelika WT St 37-2. Istraživanje niskolegirano čelika otpornog na atmosfersku koroziju aktualan je problem duži niz godina. Naime, ti čelici imaju veliku važnost za gradnju konstrukcija koje će biti izložene atmosferskim promjenama desetljećima pa čak i stoljećima. Pošto je atmosfera danas zagađenija, tj. agresivnija, važnost ovih ispitivanja je značajnija kako za izbor najpovoljnijeg materijala tako i za sigurnost konstrukcije uz ostvarenje i bitnih ekonomskih učina.

Ključne riječi: *niskouglični čelik, atmosferska korozija, otpornost na atmosfersku koroziju*

INTRODUCTION

Technical development made it possible for the metal surface corrosion to become lower by the help of already formed corrosion products, i.e. corroded layer, (as the matter of fact the widest spread method of metal protection by surface painting, but it is expensive and often technically limited).

More than 50 years ago it was started in the USA with mass production of the steel resistant to atmospheric corrosion under the title COR-TEN (COR - Corrosion, R - Resistance, TEN - Tensile strength). On the base of that, the production of the same or similar steels has been started all over the world.

Today almost all industrialized countries produce these steels, and in Germany they are known by the name: "Wetterungsbestandige Stähle" or "Korrosionsträge Stähle" [1].

However, brief and precise definition of concept for low-alloy steels resistant to atmospheric corrosion is very difficult because it is not possible to define any strict limits between these steels and those which are not. Except that, the corrosion properties depend largely on outside

so-called "micro (local) climate" influences. Nevertheless, it is possible to say that:

- these are low-alloy steels, which are different from the structural steels based on corrosion behavior. These steels, because of micro content of certain metals or residual non-metal elements (0,5 % Cu, 0,8 % Cr, 0,5 % Ni and 0,1 % P), show for the same period of time negligible loss of weight in comparison to non-alloyed steels. That means that under the influence of atmosphere a thin, stable, tightly adhered corroded layer is formed, which protects metal from further corrosion;
- low-alloy steels resistant to weather factors are not stainless materials. That's why some elements, whose quantities are unimportant, are added. Therefore, they are not able to form passive layers as high-alloyed Cr or Cr-Ni steels are;
- the period of time in which it comes to stabilization of corrosion processes, is more longer (about 2 years) for low-alloy steels and mechanism of realization of anti-corrosion protection is more complicated than for high-alloyed steels or for any other metals;
- atmosphere to which these steels are exposed must not have any harmful elements which limit the formation of corrosion protective layers, e.g. higher content of chemicals.

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CHEMICAL CONTENT AND PROPERTIES OF STEEL RESISTANT TO ATMOSPHERE CORROSION

The chemical composition of structural steels which should become resistant to atmospheric corrosion has to be chosen in such a way that the content of alloying elements, which are slowing down or stopping corrosion, is large enough. At the same time combination of carbon, manganese and other elements provide higher yield stress, good weldability, deformability and economy.

Table 1. **Chemical analysis of some low-alloyed steels resistant to atmospheric corrosion**
Tablica 1. **Kemijski sastav nekih niskolegiranih čelika otpornih na atmosfersku koroziju**

Steel grade	Country of production	Chemical analysis (max.) / % × 100								
		C	Si	Mn	P	S	Cr	Ni	Cu	V, Nb, Ti, Al, Mo, N
Coraldur 37	Austria	15	40	20/50	5	3.5	50/80	40	30/50	
Coraldur 44		15	40	40/80	5	3.5	50/80	40	30/50	
Coraldur 52		15	40	90/130	4.5	3.5	50/80	40	30/50	
Coraldur 37P		12	40	40/70	7/15	3.5	40/120	65	30/60	
Coraldur 44P		12	40	40/70	7/15	3.5	40/120	65	30/60	
Coraldur 52P		12	25/75	40/70	7/15	3.5	40/120	65	30/60	
Coraldur W		12	40	20/50	5/9	3.5	40/70	40	30/50	
WT St 37-2	Germany	13	10/40	20/50	5.0	3.5	50/80	40	30/50	
WT St 37-3		13	10/40	20/50	4.5	3.5	50/80	40	30/50	V; 2/10
WT St 52-3		15	10/40	90/130	4.5	3.5	50/80	40	30/50	
COR-TEN A	USA	12	25/75	20/50	7/155	3.5	30/125	65	25/55	
COR-TEN B		10/19	15/30	90/125	4	5	40/60		25/40	V; 2/10; Al; 1/6
COR-TEN C		12/19	15/30	90/135	4	5	40/70		25/40	V; 4/10; Al; 1/6
Republic 50		15		50/100	4	5	30	90/100	30/100	Mo: min. 10
Republic 70		20	15	100	4	4		120/150	10/150	Mo: 20/30
Hi-Steel		< 12	< 15	50/90	5/10			45/75	95/130	
AW 70-90		25	25	50	1		25	25	50	

Chemical composition of some low-alloyed steels resistant to atmospheric corrosion produced in different countries is shown in the Table 1.

Metallurgical institute in Zenica took, for examination, steel grade WT St 37-2 in accordance with DIN 17119 or S 235 JRW and with EN 10027 with chemical composition presented in Table 2. [2, 3]

Influence of microalloying elements

The improvement of non-alloyed steel grades, as it was mentioned, could be performed by alloying with certain elements, especially in small concentrations. Micro-alloyed steel grades form insoluble corrosion resistant layers, very dense and hardly stick to metal matrix.

General conclusion is that carbon up to 0.20 %, in existing quantity in low-alloyed steel grades resistant on at-

mospheric corrosion, has no essential influence in comparison with pure iron.

There is an opinion that silicon has no influence on corrosion behaviour, but some data [1] indicate that silicon decreases inclination to corrosion of non-alloyed steel grades.

Higher manganese content increases insignificantly resistance to atmospheric corrosion expect in the case when sulphur content is higher than 0,050 %.

Phosphorus addition can decrease tendency for corrosion appearance, obviously significant already at 0,050 % P, even at higher sulphur content in steel. At the same time,

phosphorus is harmful to cold mechanical working as well as on weldability.

Table 2. **Chemical composition of steel Grade S235 JRW [EN 10027]**

Tablica 2. **Kemijski sastav čelika kvalitete S 235 JRW [EN 10027]**

Steel grade	Chemical composition / %			
	C	Si	Mn	P
S235 JRW (WT St37-2)	≤ 0,13	0,10/0,40	0,20/0,50	≤ 0,050
Steel grade	Chemical composition / %			
	S	Cr	N	Cu
S235 JRW (WT St37-2)	≤ 0,035	0,50/0,80	≤ 0,009	0,30/0,50

Copper influence on corrosion resistance of steel has been well known for a long time and even 0,13 % Cu has a considerable influence.

A chromium decreases corrosion influence and at the same time it increases yield strength as well as molybdenum and nickel.

Metal corrosion

In fact, corrosion is complete etching, decaying or ruining of metal by chemical affecting. Corrosion rate and its degree depend on metal properties as well as on environment in which metal is available. We are interested in environmental factors and especially in influence of atmospheric corrosion at low-alloy steels.

Main reason for metal corrosion depends on the nature of thermo-dynamic meta-stable state, i.e. they have tendency to transform into energy more stable state forming oxides, hydroxides or similar compounds.

Small additions of alloying elements (Cu, Cr, Ni, P and so on) or their combinations make common structural steels more stable against atmospheric corrosion. This is possible because corrosion layers are formed in the period between 1 to 3 years. They are denser and stick more on metal surface than at unalloyed steels.

Such corrosion layers, consisted of different oxide-carbonates, sulphides and hydroxides, have protecting function-role and they are formed only under the certain climate condition.

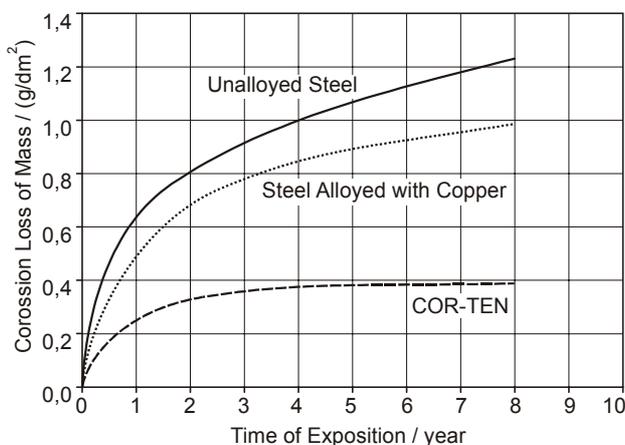


Figure 1. Corrosion losses for unalloyed steel, steel alloyed only with copper and steel resistant to atmospheric corrosion (COR-TEN) [1]

Slika 1. Korozijski gubici kod nelegiranog čelika, čelika "legiranog" samo bakrom i čelika otpornog na atmosfersku koroziju (COR-TEN) [1]

It is believed that the forming of protecting layer at steels resistant to atmospheric corrosion is finished not earlier than after 2 to 3 years, if dry and wet periods change during layers formation. The regeneration of the same layer appears at physical damage of protecting layer. Corrosion losses for unalloyed steels, alloyed steels and COR-TEN steels are presented on Figure 1.

Application of steel resistant to atmospheric corrosion

Low-alloyed steels resistant to atmospheric corrosion are covered with protecting corrosion layer, i.e. "kind-noble rust". This rust changes its colour in time from bright brown, over brown to violet-brown into nearly black-dark. Such changes give the impression that those steel are found in combination with suitable environment.

Application of these steel, besides in architecture (facades, carrying frame), is used in industrial buildings (work shops, supporting structures), in civil engineering, in pipelines, long - distance power line and railroad (car and so on), chimneys, signal devices, mine transportation equipment, river ships, oil reservoirs, wires, nails, etc.

EXPERIMENTAL PART

In Metallurgical institute in Zenica, forging and rolled products from steel grade S234 JRW (EN 10027) micro-alloyed with Ni have been produced (Table 3.). This steel

Table 3. Chemical analysis of steel
Tablica 3. Kemijski sastav čelika

Sample mark	Chemical analysis / %				
	C	Si	Mn	P	S
Melt 022039	0,09	0,52	0,37	0,035	0,035
Sample mark	Chemical analysis / %				
	Cr	Ni	Cu	Mo	ΣN
Melt 022039	0,65	0,29	0,34	0,04	0,0058

has been produced in BH Steel Iron and Steel Works and worked mechanically in Metallurgical Institute (Figure 2.).



Figure 2. Review of products from steel grade S 234 JRW
Slika 2. Izgled proizvoda od čelika S 234 JRW

On the taken samples, mechanical and metalographic examinations have been performed.

Besides the examination of mechanical properties, which have given satisfied results, for this steel grade, resistance to atmospheric corrosion has been examined under laboratory conditions [4].

Examination has been performed in accordance with DIN 50017 and DIN 50018. In the same time samples taken from straight part of products - cramps (R) and samples from curved part of cramps (S) were examined. In accordance with DIN 50018-SFW 2.05 samples surface covered with scale have been also examined.

Because of present surface scale it was not possible to have relevant results of corrosion products by scratching, so mass increase of surface unit was measured. Treating results are presented in Table 4. Marks on the samples A,

Table 4. **Mass increase on surface unit**
 Tablica 4. **Prirast mase po jedinici površine**

Sample mark	A - R	A - S	B - R	B - S	C - R
/ ((g/dm ²)/day)	0,32	0,26	0,35	0,28	0,30
Sample mark	C - S	D - R	D - S	E - R	E - S
/ ((g/dm ²)/day)	0,30	0,29	0,36	0,30	0,35

B, C, D, E are given for different dimensions of cramps (cramps length) as following: A = 440 mm, B = 490 mm, C = 540 mm, D = 590 mm, E = 640 mm.

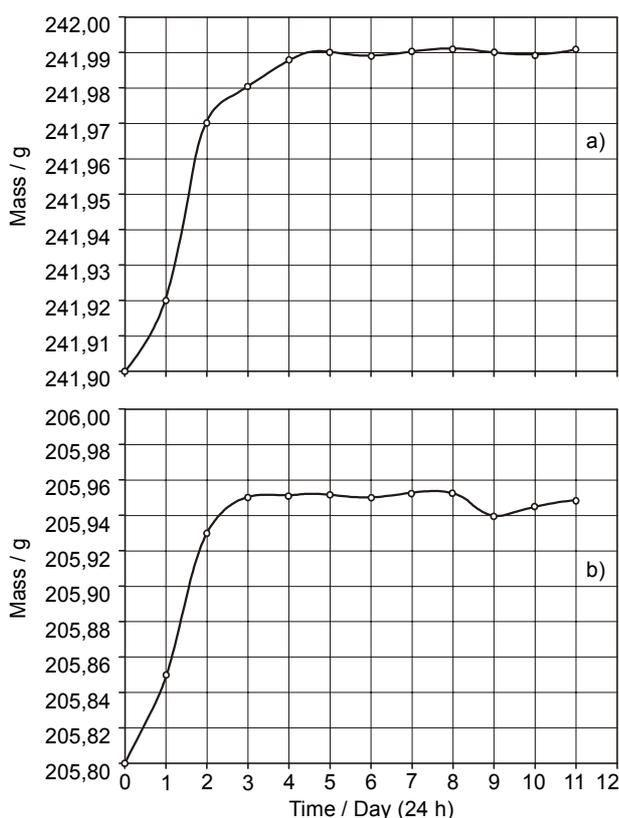


Figure 3. **Results of examination of corrosion resistance on straight part of sample (a) and curved part of sample (b) - cramp type A**

Slika 3. **Rezultati ispitivanja korozijske otpornosti na ravnom dijelu uzorka (a) i na savijenom dijelu uzorka (b) - "klamfa" tip A**

Larger differences in mass increase for the same kind of products on flat and curved part are the result of different scale thickness and textures. Namely, holding scale in condensate and atmosphere of SO₂ brings to its chemical transformation (hydration and sulphide creating). This process results in mass increase on surface unit.

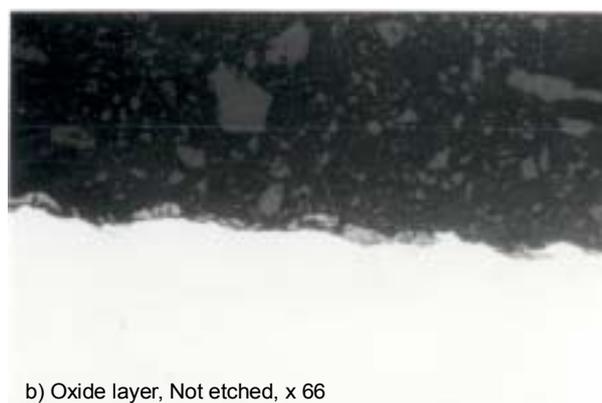
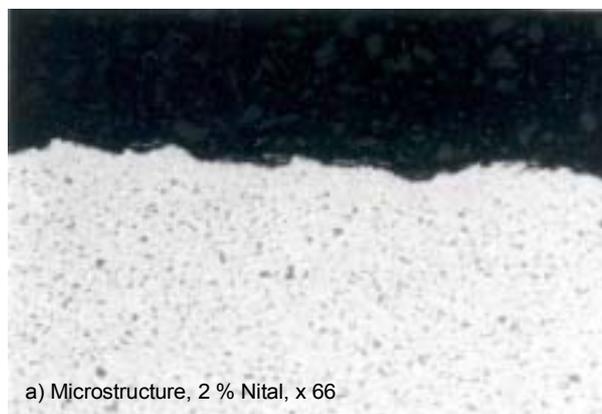


Figure 4. **Appearance of microstructure (a) and oxide layer (b) of sample in as rolled condition**

Slika 4. **Izgled mikrostrukture (a) i oksidnog sloja (b) kod uzorka nakon valjanja**

In accordance with DIN 50017 samples have been examined with cleaned surfaces in heated sulphuric acid (1:19) from which the scale had been removed. After the removing of scale, the samples have been dipped into warm nitrate acid (1:2) to remove precipitated copper from the surface, which originated from alloying additions.

On such a way, the prepared samples have been exposed to condense, as it is regulated by standard DIN 50017. Mass increase has been examined by multiplying repetitions of 24-hours cycles be possible to state the time for which corrosion product becomes compact, and after that period there begins the protection of surface from corrosion environmental effect.

The surface treatment in accordance with the mentioned standard does not assure a true image about speed of atmospheric corrosion of this steel because much more time is

needed for more complete formation of products of atmospheric corrosion. The results are presented in Figure 3.

Figure 3. shows the speed of atmospheric corrosion (given g/dm^2 , day) for a sample taken from a straight part of cramp (a) and from a curved part of cramp (b).

Mass increase between straight and curved part of the samples whose surface is descaled, is different.

But it doesn't give us a real picture because more time is needed to complete the forming of products of atmospheric corrosion. Similar diagrams are obtained for cramps type B, C, D and E - cramps with different lengths.

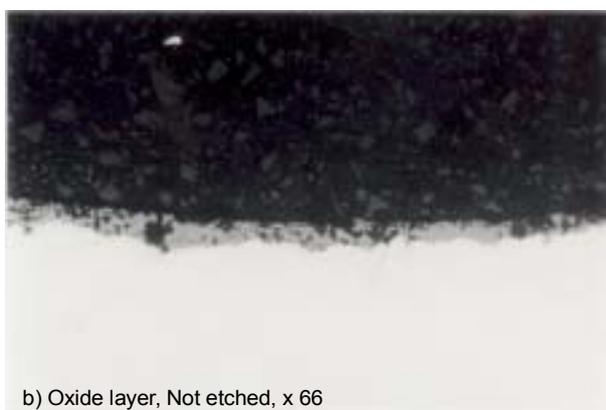


Figure 5. **Appearances of microstructure (a) and oxide layer (b) in as rolled and hot bend condition**

Slika 5. **Izgled mikrostrukture (a) i oksidnog sloja (b) kod uzorka nakon valjanja i savijanja na toplo**

By metallographical examination, high purity of metal matrix with homogenous ferrite-pearlite microstructure was established. In Figure 4. microstructure and sample edge as in rolled state is shown as well as in Figure 5. after rolling and hot bending. In the Figure 4. and 5. you can

see that oxide layer on sample edge is on the sample after rolling but you can't see it after bending.

CONCLUSIONS

The results of proper examination of corrosion resistance of steel grade WT St 37-2 show the following:

1. On the samples of experimental strips after rolling and bending in as heated state, corrosion process performed by treatment in distillate and deionized water in accordance with DIN 50017 is stopped on 4th cycle (one cycle last 24 hours).
2. At strip samples after cold bending corrosion, process is stopped in 6th cycle. (Figure 3.).
3. Mass increase, during the examination of the corrosion resistant process in accordance with DIN 50018 on strips (A-R, B-R, C-R, D-R, E-R) in as rolled condition, is $0.28 \text{ g}/\text{dm}^2$ and on strips (A-S, B-S, C-S, D-S, E-S) after bending is $0.30 \text{ g}/\text{dm}^2$.
4. This confirms that corrosion resistance is satisfied still after mechanical working although a bit higher, what is in accordance with concentration of stresses and their negative influence on corrosion process.
5. Otherwise, diagrams show that after the intensive beginning of the corrosion process it stops, i.e. steel is then covered with protecting layer, which protects steel from further damaging.
6. These are experimental and fastened conditions of the origin of corrosion and they are always higher than the real ones but they represent important data.
7. It is possible to get real results after exposing samples or structural parts to changeable climate conditions for longer period of time, i.e. for several year.

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